

学校编码: 10384

密级_____

学号: 22420091151127

厦 门 大 学

硕 士 学 位 论 文

厦门湾海水-沉积物系统中 PCDD/Fs 的含量、 多相分配及颗粒垂直通量研究

Concentration, Multi-phase Partitioning and Vertical Fluxes
of PCDD/Fs in Seawater-Sediment System of Xiamen Bay

洪 清 泉

指导教师姓名: 蔡明刚 副教授

专 业 名 称: 海 洋 化 学

论文提交日期: 2012 年 05 月

论文答辩时间: 2012 年 05 月

2012 年 06 月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下，独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果，均在文中以适当方式明确标明，并符合法律规范和《厦门大学研究生学术活动规范（试行）》。

另外，该学位论文为（ ）课题（组）的研究成果，获得（ ）课题（组）经费或实验室的资助，在（ ）实验室完成。（请在以上括号内填写课题或课题组负责人或实验室名称，未有此项声明内容的，可以不作特别声明。）

声明人（签名）：

王清东

2012年6月12日

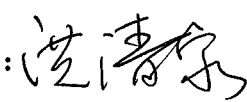
厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

- () 1. 经厦门大学保密委员会审查核定的保密学位论文，
于 年 月 日解密，解密后适用上述授权。
(☒) 2. 不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

2012 年 6 月 12 日

目 录

摘要	I
ABSTRACT	III
缩略词表	VI
图目录	VIII
LIST of FIGUREs	XI
表目录	XIV
LIST of TABLEs	XVI
第一章 绪论	1
1.1 研究意义	1
1.1.1 持久性有机污染物概述	1
1.1.2 环境中 POPs 的来源、迁移转化和归宿概述	3
1.1.3 PCDD/Fs 概述	4
1.1.4 河口区海水-沉积物系统中 POPs 动力学过程的研究意义	8
1.1.5 我国开展该领域研究的意义	9
1.2 海水及沉积物中 PCDD/Fs 的国内外研究现状	10
1.2.1 海水中 PCDD/Fs 的研究现状	10
1.2.2 沉积物 PCDD/Fs 的研究现状	13
1.2.3 PCDD/Fs 的源解析研究概述	16
1.2.4 PCDD/Fs 多介质动力学及模型研究现状	17
1.3 主要研究目的和研究内容	19
1.3.1 主要研究目的	19
1.3.2 主要研究内容	19
第二章 样品采集、分析与模型计算方法	21
2.1 研究区域概况	21
2.1.1 气候状况	21

2.1.2 水动力条件概况	21
2.1.3 地形地貌特征	22
2.1.4 泥沙	22
2.2 采样站位和样品采集	23
2.3 PCDD/Fs 的分析	25
2.3.1 材料与试剂	25
2.3.2 PCDD/Fs 样品前处理	28
2.3.3 仪器分析	30
2.3.4 质量控制与质量保证 (QA/QC)	31
2.4 水体基本参数的分析	34
2.5 水体 ^{234}Th 的分析	36
2.6 水体 ^{238}U 的计算	36
2.7 沉积物理化性质分析	36
2.7.1 沉积物 ^{210}Pb	36
2.7.2 沉积物粒度	37
2.7.3 沉积物 TOC 和 BC	37
2.7.4 沉积物干密度	37
2.8 计算模型简介	37
2.8.1 水体中 PCDD/Fs 的多相分配	38
2.8.2 水体颗粒载带的 PCDD/Fs 垂直输出通量的估算	40
2.8.3 沉积物沉积速率 (S_0) 及 PCDD/Fs 埋藏通量 (F_{bu}) 的估算	41
2.8.4 沉积物中 PCDD/Fs 向上覆水的颗粒再悬浮通量 (F_{res})	42
第三章 海水参数的分布特征	43
3.1 海水基本参数的水平分布特征	45
3.1.1 温度、盐度、SPM	45
3.1.2 Chl- α	45
3.1.3 pH、DOC 和 POC	48
3.2 海水基本参数的垂直分布特征	50
3.2.1 温度、盐度、SPM	50

3.2.2 Chl- <i>a</i>	51
3.2.3 pH、DOC 和 POC	52
第四章 海水中 PCDD/Fs 的分布与分配	55
4.1 海水中 PCDD/Fs 的含量和 TEQ	55
4.1.1 颗粒态 PCDD/Fs 的含量和 TEQ	55
4.1.2 表观溶解态（胶体态+自由溶解态）PCDD/Fs 的含量和 TEQ	63
4.1.3 总 PCDD/Fs 的含量和 TEQ	65
4.2 海水中 PCDD/Fs 的分布	65
4.2.1 海水中 PCDD/Fs 的水平分布	65
4.2.2 海水中 PCDD/Fs 的垂直分布	70
4.3 海水中 PCDD/Fs 的同系物组成与输入途径	74
4.4 海水中三相间 PCDD/Fs 的分配及影响因素	76
4.4.1 颗粒态和表观溶解态间 PCDD/Fs 的分配	76
4.4.2 三相间 PCDD/Fs 的分配	83
4.4.3 影响三相间 PCDD/Fs 的分配的因素探讨	83
第五章 沉积物中 PCDD/Fs 的时空分布	90
5.1 表层沉积物中 PCDD/Fs 的分布	90
5.1.1 表层沉积物 PCDD/Fs 的含量与毒性当量	90
5.1.2 表层沉积物中 PCDD/Fs 及其毒性当量的分布	91
5.2 柱状沉积物中 PCDD/Fs 的分布	96
5.2.1 柱状沉积物的沉积物速率	96
5.2.2 柱状沉积物中 PCDD/F 的含量与毒性当量	96
5.2.3 柱状沉积物中 PCDD/F 的分布	97
5.3 沉积物中 PCDD/F 的同系物组成特征及来源	99
5.4 沉积物性质对 PCDD/Fs 分布的影响	100
5.4.1 粒度分布的影响	100
5.4.2 总有机碳（TOC）和炭黑（BC）的影响	103
第六章 海水-沉积物界面颗粒 PCDD/Fs 交换通量	112

6.1 水体中颗粒 PCDD/Fs 的垂直输出通量	112
6.1.1 表层水中颗粒态 PCDD/Fs 的垂直输出通量	113
6.1.2 水柱中 PCDD/Fs 的垂直输出通量	113
6.1.3 PCDD/Fs 的垂直输出通量与水化学参数的关系	115
6.2 沉积物中 PCDD/Fs 的埋藏通量	115
6.3 沉积物中 PCDD/Fs 的再悬浮通量	118
6.4 海水-沉积物界面颗粒 PCDD/Fs 交换通量	118
第七章 总结与展望	121
7.1 主要研究结果	121
7.2 主要创新点	122
7.3 不足与展望	123
参考文献	124
攻读硕士学位期间发表论文	151
会议摘要	152
参与科研项目与现场科考	153
致谢	154

CONTENT

Abstract (In Chinese)·····	I
Abstract (In English) ·····	III
Abbreviations ·····	VI
List of Figures (In Chinese) ·····	VIII
List of Figures (In English)·····	XI
List of Tables (In Chinese) ·····	XIV
List of Tables (In English)·····	XVI
Chapter 1 Introduction ·····	1
1.1 Research Significance ·····	1
1.1.1 General Properties of Persistent Organic Pollutants (POPs) ·····	1
1.1.2 Summary on the Source and Fate of POPs in the Environment ·····	3
1.1.3 Summary of PCDD/Fs ·····	4
1.1.4 Significance on the Dynamics of POPs in Seawater-Sediment System in Estuarine and Coastal Area ·····	8
1.1.5 Significance to Carry Out Research in This Field in China ·····	9
1.2 Research Advances on PCDD/Fs in Seawater and Marine Sediment around the World ·····	10
1.2.1 Research Advances of PCDD/Fs in Seawater ·····	10
1.2.2 Research Advances of PCDD/Fs in Marine Sediment ·····	13
1.2.3 Research Advances on the Source Analysis of PCDD/Fs ·····	16
1.2.4 Research Advances on the Dynamics and Modelling of PCDD/Fs ·····	17
1.3 Objectives and Contents ·····	19
1.3.1 Research Objectives ·····	19
1.3.2 Research Contents ·····	19
Chapter 2 Sampling, Analysis and Modelling ·····	21

2.1 Review of the Study Area	21
2.1.1 Climate	21
2.1.2 Hydrological Conditions	21
2.1.3 Topography	22
2.1.4 Sediment	22
2.2 Sampling Site and Sampling Method	23
2.3 Analysis of PCDD/Fs	25
2.3.1 Material and Reagent	25
2.3.2 Pretreatment of Samples	28
2.3.3 Instrumental Analysis	30
2.3.4 Quality Assurance and Quality Control (QA/QC)	31
2.4 Analysis of Basic Parameters in Seawater	34
2.5 Analysis of ^{234}Th in Seawater	36
2.6 Calculation of ^{238}U in Seawater	36
2.7 Analysis of Sediment Characteristics	36
2.7.1 ^{210}Pb	36
2.7.2 Grain Size	37
2.7.3 TOC and BC	37
2.7.4 Dry Density	37
2.8 Brief Description of the Research Model	37
2.8.1 Multi-phase Partitioning of PCDD/Fs in Seawater	38
2.8.2 Sinking Flux of Particulate PCDD/Fs in Seawater	40
2.8.3 Sedimentation Rate (S_0) and Burial Flux (F_{bu}) of PCDD/Fs in Sediment	41
2.8.4 Resuspension Flux (F_{res}) of PCDD/Fs to Overlying Seawater	42
Chapter 3 Distribution of the Basic Parameters in Seawater	43
3.1 Spatial Distribution of Basic Parameters in Seawater	45
3.1.1 Temperature, Salinity and SPM	45
3.1.2 Chl- <i>a</i>	45
3.1.3 pH, DOC and POC	48

3.2 Vertical Profile of Basic Parameters in Seawater·····	50
3.2.1 Temperature, Salinity and SPM·····	50
3.2.2 Chl- <i>a</i> ·····	51
3.2.3 pH, DOC and POC·····	52
Chapter 4 Distribution and Partition of PCDD/Fs in Seawater·····	55
4.1 Concentrations and TEQ in Seawater·····	55
4.1.1 Particulate PCDD/Fs·····	55
4.1.2 Apparently Dissolved (Colloidal and Freely Dissolved) PCDD/Fs·····	63
4.1.3 Total PCDD/Fs·····	65
4.2 Distribution of PCDD/Fs in Seawater·····	65
4.2.1 Spatial Distribution·····	65
4.2.2 Vertical Profile·····	70
4.3 Congener Pattern and Potential Source of PCDD/Fs in Seawater·····	74
4.4 Partition in the Three-phase System and Potential Reason·····	76
4.4.1 Distribution between Particulate and Apparently Dissolved Phase·····	76
4.4.2 Partition between Particulate, Colloidal and Freely Dissolved Phase·····	83
4.4.3 Potential Factors Controlling the Partition in the Three-phase System·····	83
Chapter 5 Spatial and Temporal Distribution of PCDD/Fs in Sediment·····	90
5.1 Spatial Distribution of PCDD/Fs in the Surface Sediment·····	90
5.1.1 Concentrations and TEQ of PCDD/Fs·····	90
5.1.2 Spatial Distribution of the Concentration and TEQ·····	91
5.2 Temporal Distribution of PCDD/Fs in Core Sediment·····	96
5.2.1 Sedimentation Rate·····	96
5.2.2 Concentrations and TEQ·····	96
5.2.3 Temporal Distribution of PCDD/F·····	97
5.3 Congener Pattern and Potential Source of PCDD/Fs in Sediment·····	99
5.4 Influence of Sediment Characteristics on PCDD/Fs in Sediment·····	100
5.4.1 Grain Size·····	100
5.4.2 TOC and BC·····	103

Chapter 6 Vertical Dynamics of Particle Bounded PCDD/Fs in the	
Seawater–Sediment Interface	112
6.1 Vertical Sinking Flux of Particulate PCDD/Fs in Seawater	112
6.1.1 Export Fluxes of PCDD/Fs from Surface Seawater	113
6.1.2 Sinking Fluxes of PCDD/Fs from Seawater Column	113
6.1.3 Relationship between Vertical Flux of Particulate PCDD/Fs and	
Seawater Chemistry Parameters	115
6.2 Burial Flux of PCDD/Fs to Bottom Sediment	115
6.3 Resuspension Flux of PCDD/Fs from Sediment to Seawater	118
6.4 Exchange Flux of Particulate PCDD/Fs in the Seawater-Sediment Interface	118
Chapter 7 Conclusions and Future Perspectives	121
7.1 General Conclusions	121
7.2 Main Innovation	122
7.3 Shortage and Future Perspectives	123
References	124
Publications	151
Conference Paper	152
Programmes and Field Work	153
Acknowledgement	154

摘要

于 2011 年 12 月采集了厦门湾海水、沉积物样品,开展海水-沉积物系统中多氯代二苯并二噁英/呋喃 (Polychlorinated dibenzo-*p*-dioxins and dibenzofurans, PCDD/Fs) 的多相分配及颗粒垂直通量研究。首次获得 PCDD/Fs 在厦门湾海水中悬浮颗粒态、胶体态 (DOC 吸附态) 和自由溶解态的含量、水平与垂直分布,沉积物中 PCDD/Fs 的时空分布, PCDD/Fs 的来源和海水-沉积物界面颗粒态 PCDD/Fs 的垂直交换通量等特征,提升了对海洋环境中 PCDD/Fs 的多相分配和颗粒垂直交换过程的认识。取得了以下成果:

厦门湾水体中 17 种 PCDD/Fs 的总含量(PCDD/Fs)为 35.389-283.933 pg/L, 平均为 145.156 pg/L。其中, PCDDs 含量为 34.929-282.554 pg/L, 占 PCDD/Fs 的 98.6-99.6%。总体上, 厦门湾水体中的 PCDD/Fs 含量处于较高水平。水体中 PCDD/Fs 的总毒性当量 (采用 WHO 2005 年的毒性当量因子体系计算) 为 0.084-0.422 pg TEQ/L (平均为 0.250 pg TEQ/L), 超过美国 EPA 规定的水质标准 (0.14 pg TEQ/L)。其中, 对毒性当量贡献最大的为 1,2,3,7,8-P₅CDD, 其次为 O₈CDD 和 1,2,3,4,6,7,8-H₇CDD。

表层水体中 PCDD/Fs 的含量随着与九龙江口距离的增大而减小, 表明九龙江水体输入是研究区域 PCDD/Fs 的主要输入途径。垂直水体中 PCDD/Fs 呈现上层水体和底层水体含量较高而中层水体含量较低的分布, 主要与载带 PCDD/Fs 的悬浮颗粒物在水体中的迁移有关。上层水体主要载带大量颗粒物的九龙江水体输入, 因而具有较高的 PCDD/Fs 含量, 底层水体则主要由于沉积物的再悬浮作用从沉积物释放颗粒态 PCDD/Fs。

水体中的 PCDD/Fs 在悬浮颗粒态-胶体态-自由溶解态三相间主要以悬浮颗粒态存在, 占 98.4-99.7%, PCDD/Fs 在颗粒物与表观溶解态间的分配接近平衡。PCDD/Fs 在三相间的分配是温度、盐度、pH、Chl-*a*、DOC、SPM、POC/SPM 等因素共同作用的结果。其中, POC/SPM、Chl-*a*、pH 和 DOC 主要控制胶体态和自由溶解态间的分配, SPM 主要控制颗粒态的含量与分配。

厦门湾沉积物 PCDD/Fs 的含量为 1 129.656-3 806.936 pg/g d.w., 平均含量为 1 809.188 pg/g d.w., 总毒性当量为 1.60-6.65 pg TEQ/g, 平均为 2.49 pg TEQ/g,

其毒性当量主要以五至八氯代的 PCDDs 贡献为主。根据 Hemming 等 (2003) 提出的生物毒性风险评价标准, 厦门湾表层沉积物中 PCDD/Fs 含量对生物没有毒性风险。沉积物中 PCDD/Fs 含量与沉积物中的细颗粒 (粘土、粉砂) 和 TOC 含量存在正相关关系, 说明沉积物中 PCDD/Fs 主要受细颗粒和 TOC 吸附作用控制。

表层沉积物中 PCDD/Fs 的分布与水体中颗粒态 PCDD/Fs 的分布相似, 从河端至海端逐渐降低, 说明九龙江水体载带的颗粒态 PCDD/Fs 往外海迁移过程中的沉降和埋藏是沉积物中 PCDD/Fs 的主要来源。对柱状沉积物的研究表明, 在百年时间尺度上, PCDD/Fs 呈现波动变化, 最大值出现在 1970 年代, 时间变化主要与 PCP 等化学品的生产与使用的变化有关。

海水和沉积物中 PCDD/Fs 的同系物组成相似, 均以 O_8CDD 为主, 其次为 H_7CDD , 另有少量 O_8CDF 和 H_7CDF 。结合主成分分析和聚类分析, 判断厦门湾 PCDD/F 的主要来源是 PCP 及其钠盐使用过程中杂质所含的 PCDD/Fs 的排放及污水污泥的输入, 其主要输入途径是通过污水污泥汇入九龙江水体, 并随九龙江水体输送, 大气沉降所占的比例很小。百年时间尺度上, PCDD/Fs 的同系物组成几乎不变, 说明近 100 年内, PCDD/Fs 降解作用不显著。

对海水-沉积物界面颗粒 PCDD/Fs 的垂直交换通量估算表明, 水平输送和沉积物的埋藏作用是 PCDD/Fs 从海水-沉积物界面输出的主要过程。在扩散作用和降解作用可以忽略的条件下, 河口区沉积物再悬浮通量不能忽略, 证明了河口区沉积物为 PCDD/Fs 的“二次污染源”。

关键词: 二噁英; 海水-沉积物; 多相分配; 通量; 埋藏与再悬浮; 厦门湾

ABSTRACT

Seawater and sediment samples in the Xiamen Bay were collected in December, 2011, aiming to study the multi-phase partitioning and vertical fluxes of particle bounded polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in an estuarine seawater-sediment system. It's the first time to report the partitioning between particulate-colloidal (DOC bounded)-freely dissolved phase, horizontal and vertical distribution pattern in seawater, spatial and temporal distribution in sediment and vertical fluxes of particle particle bounded PCDD/Fs. It makes a great improvement in understanding the particulate dynamics and multi-phase behavior of PCDD/Fs in marine environment. Main conclusions are as followed:

The sum concentrations of seventeen PCDD/F congeners in seawater of the Xiamen Bay were ranged in 35.389-283.933 pg/L (averaged in 145.156 pg/L), which means they were in the higher end of the PCDD/Fs levels all over the world. The sum concentrations of PCDDs were ranged in 34.929-282.554 pg/L, contributing 98.6-99.6% of PCDD/Fs. The TEQ (calculated with the WHO 2005 Toxic Equivalency Factors) were in the range of 0.084 to 0.422 pg TEQ/L, with an average of 0.250 pg TEQ/L. This means the TEQ in seawater of the Xiamen Bay exceed the water quality criteria recommended by USEPA. Contribution to TEQ for congeners was in the order: 1,2,3,7,8-P₅CDD>O₈CDD>1,2,3,4,6,7,8-H₇CDD.

The concentrations in the surface seawater decreased with the distance from the Jiulong River Estuary, indicating a potential input from the river. Lower concentrations existed in the median layer of the seawater, while higher ones distributed in the surface and the bottom seawater in the vertical profile. This involved the transport of particles bounded PCDD/Fs in water column. A large amount of particle containing PCDD/Fs was input from the Jiulong River, leading to the higher concentrations in the surface seawater while the resuspension of sediment resulted to higher concentrations in the bottom seawater

A three-phase (particulate-colloidal-freely dissolved phase) partitioning model

was applied and found that particle bounded PCDD/Fs contributed 98.4-99.7% of the PCDD/Fs in seawater. The distribution between particulate and apparently dissolved phase was found to be near or at equilibrium. The partition in the three-phase system may result from a combination of the effects of temperature, salinity, pH, Chl-*a*, DOC, SPM and POC/SPM. The content and partitioning in the particles was dominated by SPM, while the partitioning between the colloidal phase and freely dissolved phase was controlled by the combined effects of POC/SPM, Chl-*a*, pH and DOC.

The concentrations and TEQ of PCDD/Fs in the sediment of Xiamen Bay were ranged in 1 129.656-3 806.936 pg/g d.w. (averaged in 1 809.188 pg/g d.w. and 1.60-6.65 pg TEQ/g d.w. (averaged in 2.49 pg TEQ/g), respectively. The TEQ was mainly contributed by *penta-* to *octa-* chlorinated congeners, which caused no risk to organisms. Significant positive relationships between fine-grained sediments, organic carbon and PCDD/Fs indicated that sorption of PCDD/Fs to organic matter and fine particles dominates the fate of PCDD/Fs in the sediments.

The PCDD/Fs in the surface sediments demonstrated a similar distribution with that in the surface seawater, decreasing from the Jiulong River Estuary to the outer of the bay, which implied a deposition and burial of particulate PCDD/Fs from overlying seawater. The temporal distribution in the core sediment fluctuated in the time scale of 100 years, with a maximum in the 1970s, which was due to the change in the manufacture and use of chemicals such as PCP.

Similar congener patterns in the seawater and sediment were found to be dominated by O₈CDD, which is followed by H₇CDD and minor O₈CDF and H₇CDF. The congener patterns, combined with the results of Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA), indicated a potential major source from the impurity of PCP (Pentachlorophenol)+its sodium and sewage sludge. The main path is the input of sewage sludge and the transport of Jiulong River water. The congener pattern did not change over 100 years, implying essentially zero degradation had occurred in the environment.

The estimated vertical fluxes of particulate PCDD/Fs in the seawater-sediment interface indicated that horizontal transport and sediment burial are the dominant

export processes. Without the consideration of diffusion and degradation, the resuspension flux should not be ignored in estuary which makes estuarine sediments potential secondary source of PCDD/Fs.

Keywords: Dioxin; Seawater-sediment; Multi-Phase Partitioning; Flux; Burial and Resuspension; Xiamen Bay

Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to etd@xmu.edu.cn for delivery details.

厦门大学博硕士论文摘要库